

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Picosecond Time Resolved X-ray Scattering of trans-Dibromoethylene and trans-Stilbene in non polar Solvents: Probing Solvent-Supported Large Amplitude Motion	Experiment number: SC-681
Beamline:	Date of experiment: (might be not correctly reminded) from: 05/07/00 to: 10/07/00	Date of report: 06/03/01
Shifts:	Local contact(s): F. Schotte	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): *Techert, Simone (1,2) Old Address: (1) ESRF, BP 220, 38043 GRENOBLE CEDEX New Adress: (2) Max Planck Institute for Biophysical Chemsitry, Dep. 010, 37070 Goettingen, Germany Zachariasse, Klaas (2) & Wulff, Michael (1)		

Report:

If a chemical system is electronically excited e.g. by absorbing an optical photon the shape of the potential energy surface (PES) of the excited state can significantly differ from the ones of the ground state. The change of the PES landscape is expressed in the formation of new little "valleys" or "hills". These "local perturbations" arise if the PES of the excited state is similar in energy to another PES of another electronic excited state - requiring particular resonance conditions for a selected geometry of the system (see also Wiegner theorem). Compared to the PES of a ground state, the PES of the excited state is only populated as long as the photon is absorbed which is typically in the order of picoseconds to sub-microseconds. Therefore time-resolved (TR) x-ray diffraction is one method of choice in order to characterise which geometry is dominantly formed after the absorption of optical light (see e.g. fig1, left). The TR methods help to evaluate time-scale and structure of the transient species during the complex decay process.

In experiment No SC-681 (together with experiment No SC-504 (1999), see also the corresponding report) we studied TR powder diffraction of *N,N*-dimethylaminobenzonitrile (DMABN, $C_9H_{10}N_2$, fig1), a compound widely discussed in literature with emphasis on relaxation mechanisms during photo-excitation [1-4]. Our aim was to measure the structural relaxation following photo-excitation and to test the feasibility of using this method to determine displacements at atomic resolution on a picosecond timescale. One of the main questions was whether structural relaxation takes place in a crystal and, if so, what are the amplitude and timescale. With TR x-ray diffraction it should be possible to distinguish between the inversion motion of the CH_3 -groups around the N-atom and the torsional motions of the CH_3 -groups as relaxation processes on the excited state PES (fig1). Depending on the kind of motions, electronic coupling effects between the π electrons (torsion) or vibronic coupling as in NH_3 (inversion) characterize the photo-physical behavior of DMABN.

In SC-681 we could show, that it is possible to characterise transient structures in the solid state by TR x-ray powder diffraction [5-7]. Some results of these experiments are summarised in fig1. In fig1, right the decay time of the transiently formed averaged torsional angle is shown. Clearly, the averaged torsional angle could be resolved in space and time and was found to be 10° in maximum. The hole relaxation process of the photo-excited solid can be summarised by a - non-expected - coupled motion of inversion and torsion.

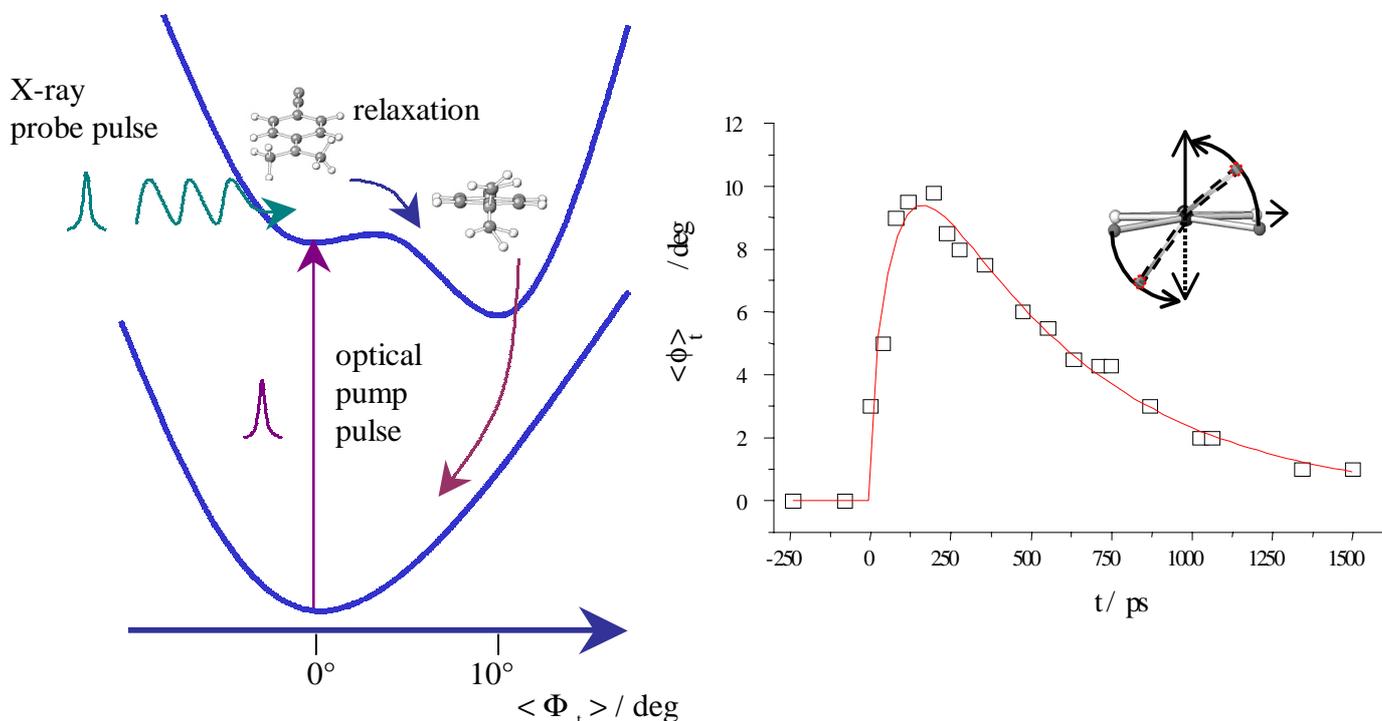


Fig 1: Left: Principle of TR x-ray diffraction on the PES of photo-excited DMABN crystals. Right: Experimental decay time of the averaged torsional angle ϕ_{tors} in the solid state [5,6]. C-atoms of the phenyl moiety are given as open, N-atoms as black and the amino-C as grey circles. Note, that the H-atoms are not shown, since they do not contribute to the x-ray diffraction signal.

References:

- [1] E. Lippert, *Z. Naturforsch.* **10 A**, 541 (1955).
- [2] K. Rotkiewicz, K. H. Grellmann and Z. R. Grabowski, *Chem. Phys. Lett.* **19**, 315 (1973);
- [3] W. Rettig, *Angew.Chem.Int. Ed. Engl.* **25**, 971 (1986).
- [4] C. Chudoba, A. Kummrow, J. Dreyer, J. Stenger, E. T. J. Nibbering, T. Elsaesser and K. A. Zachariasse, *Chem. Phys. Lett.* **309**, 357 (1999).
- [5] S. Techert, F. Schotte and M. Wulff, *Phys. Rev. Lett.* **86 (10)**, 2030 (2001); C. Day in *Phys.Tod.* **3** (2001).
- [6] S. Techert, F. Schotte and M. Wulff, *Highlights of the ESRF* **2000**, 14 (2001).
- [7] F. Schotte, S. Techert, P. Anfinrud, V. Srajer, K. Moffat and M. Wulff, in: "Handbook of Synchrotron Radiation", Ed. D. Mills, Wiley and Sons, in press (2001).
- [8] S. Techert, F. Schotte and M. Wulff, *Highlights of the ESRF* **1999**, 12 (2000).